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MISSILE VAPOR DETECTION

SYSTEMS

DDC

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MISSILE SAFETY DIVISION
DIRECTORATE OF AEROSPACE SAFETY
DEPUTY THE INSPECTOR GENERAL, USAF
NORTON AFB, CALIFORNIA

(6) MISSILE VAPOR DETECTION

SYSTEMS ,

ENGINEERING PROJECTS BRANCH

MISSILE SAFETY DIVISION

DIRECTORATE OF AEROSPACE SAFETY

NORTON AFB, CALIFORNIA

ABSTRACT

This study describes the physical methods now used
with Air Force ballistic missile systems to detect
hazardous vapors, the limitations of these methods as
spill and leak detectors, and future developments in
the field of automatic detection of spills and leaks.
Emphasis is placed on the safety objectives of spill and
leak detection systems. Recommendations are given
concerning vapor detection system selection criteria,
technical data and training, remedial measures for current
systems, and future developments.

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INTRODUCTION

I. This study deals with an evaluation of the physical principles used to automatically detect the presence of spills and leaks of missile propellants and other hazardous fluids. A good design supported by a preventive maintenance program that takes cognizance of inspection, maintenance and replacement requirements will minimize this potential hazard. The first task is to prevent spills and leaks. However, it is recognized that all leaks and spills cannot be prevented.

A gasket fails, a connection is improperly installed, lines, valves, and tanks are damaged, or a discrepancy is overlooked. These are but a few examples of why a leak or bulk spillage may occur. If it does occur it may result in contamination, fire, damage to equipment, malfunction of components, and/or injury to personnel. The toxic, flammable and/or explosive properties of missile propellants, and hydrocarbons used in diesel generators and hydraulic systems, makes early detection of such incidents very important. Early detection allows prompt remedial action to be taken to prevent or limit the damage. Automatic leak or spill detection systems should therefore be an inherent safety consideration in any missile weapon system containing hazardous liquids.

The safety objectives of a spill or leak detection system are:

1. Reliably detect the "abnormal" presence of the hazard.

2. Immediately activate the warning system when a leak or spill occurs.

3. Identify the source of the leak.

4. Record the quantitative level of vapor concentration.

In order for these objectives to be met the system should be continuous in operation, afford complete coverage of the area, and be sensitive and selective to the vapors involved.

The purpose of this study is to:

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1. Point out some of the limitations of vapor detection system used in Air Force missile systems.

2. Recommend actions which will eliminate present deficiencies to assure that the safety objectives discussed herein will be provided for in future systems. These recommendations will be brought to the attention of responsible agencies by separate correspondence.

Information contained in this study was gathered from a review of technical data (see Bibliography) and field reports, discussions with equipment manufacturers, Ballistic Systems Division, and Rocket Propulsion (Edwards AFB) Lab personnel.

II. RECOMMENDATIONS

A. Vapor Detection System Selection

1. That vapor detection systems be specified to have the sensitivity to detect the range of vapor concentrations which can exist when a spill or leak occurs. **(Ref para IIIB7c)**

2. That the detection devices selected be capable of adequate selectivity for the various hazardous substances in the system. (Ref para IIIB7d)

3. That point sampling systems be provided with sufficient sniffers to insure immediate pickup of leaks. (Ref para IIIB1b)

4. That a test program be developed to validate the effectiveness of a selected detection system in a facility before a system is installed in similar facilities. (Ref para IIIB6)

5. That, if possible, utilize fuel and oxidizer vapor detectors within a weapon system which operate on the same principle. (Ref para IIIB7c)

6. That, if possible, methods requiring the use of liquid cells (electrolytes) not be used. (Ref para IIIB1b,c)

B. Technical Data Training

1. That part of the test program objectives be to develop the maintenance required to keep the system operational as well as the training, skills, technical data and material requirements to support a good maintenance program on detection systems. (Ref para IIIB2 and IIIB6)

2. That adequate technical data coverage and training on maintenance of the equipment is provided prior to installing the detection system. (Ref para IIIB2a)

3. That the Air Force acquire an internal capability to train operational and maintenance personnel. (Ref para IIIB2b)

C. Remedial Measures for Current Systems

1. That flanges, valves, and all other suscep-
tible leakage points be taped or painted with a colorometric
chemically treated paint or tape for quick identification
of a leak point. If these tapes and paints are not avail-
able, they should be developed for AF use. (Ref para IIIB3b)

2. That a test be established to determine the
minimum concentrations detectable by infrared devices now
being used. Subsequent to this test, consideration be
given to use the infrared principle for detection of aero-
zine and nitrogen tetroxide. (Ref para IIIB7b and c)

3. That a study be initiated to determine if
sniffer points are properly located and whether additional
sniffers are required. (Ref para IIIB3a and b)

4. That a study be conducted to determine the
best method to continuously detect RP-1, diesel fuel and
lubricating oils, and hydraulic fluid spills and leaks.
Both vapor detection, liquid level and flow principles
should be evaluated.

D. Future Developments

1. That development work continue on the appli-
cation of area detection methods. (Ref para IIIC1)

2. That future liquid level sensing applications
as used for transfer of propellant, tanking and detanking,
etc., be designed to incorporate warning signals for spill
and leak detection purposes. (Ref para IIIC2)

3. That future liquid level sensing systems use
methods whereby the detector system is situated outside
the containment vessel. (Ref para IIIC2e)

4. That spill and leak detection devices be
developed for high pressure hydraulic fluid systems and
diesel generator fuel systems.

III. ANALYSES

A. Principles of Operation

The principles of operation covered herein include thermal conductivity, catalytic combustion, depolarization, paramagnetic thermal, ionization and infrared absorption and coulametric titration. Other methods used in some portable detection instruments will also be mentioned. Table I lists the vapor detection system principles currently used for liquid propulsion ICBMs. Table II briefly describes these principles. Appendix A describes these methods in more detail.

These detection systems were designed to monitor the environment within ICBM Launcher and Propellant Storage facilities to warn of the presence of toxic vapors or if flammability was the major hazard, to warn of concentrations of vapors approaching combustible levels. The general operational requirements of these systems were that they monitor susceptible areas and if limits were exceeded automatically activate remote audible and visual warning, air purge, water fog and deluge systems. All the installed systems described herein include suction pumps which draw (sniff) samples of air (a station selector permits sequential monitoring of multiple stations) through copper or plastic tubing located between the selected areas and the detector cell. An analyzer cabinet houses the detector cell and circuits (wheatstone bridge, relays, amplifiers, etc.) required to provide the output signals to the warning and control systems mentioned above. As many of these methods use a wheatstone bridge for output signal purposes, Appendix B is provided to describe how this functions. All of the methods of gas and vapor analysis utilize physical principles of operation and require empirical calibrations.

B. Limitations

The vapor detection methods described herein fall somewhat short of filling all of the objectives of a good spill and leak detection system.

1. Continuous Operation: The present systems are designed for continuous operation; however, the term continuous is not realistic. The detection system does not operate on a 24 hour basis because:

    a. The equipment must be calibrated frequently.

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b. Chemical cells and electrode, filters, etc., must be periodically replaced. Electrical components which burn out or malfunction such as relays, amplifiers, resistors must also be replaced.

c. Electrolyte, reagents, calibration span gas, must be maintained or completely replenished, at correct levels.

d. When the system begins to drift or malfunction, troubleshooting and recalibrating the system can be a time consuming operation.

e. To correct malfunctions a thorough understanding of the system is mandatory. Lack of troubleshooting and repair ability is synonymous with excessive down time.

f. Lack of spare parts support will shut down system operation.

g. The monitoring operation is intermittent rather than continuous because of the sequential sampling of sniffer points. Each station of an eight station analyzer set is only sampling for 30 seconds every four minutes.

2. Maintenance Training:

a. Many examples could be cited which point out that these systems are fairly complex and require specialized care. Technicians therefore must be adequately trained in operation, calibration, and periodic maintenance, troubleshooting, check out and repair. Otherwise, the equipment will break down, or malfunction. Technical data must adequately cover all these areas. A malfunction could have serious implications. For example: faulty maintenance or operation has resulted in electrical shorts which have activated water deluge or fog systems; in other cases erroneous readings caused by system drift or faulty calibration may result in delays and confusion.

b. Training of maintenance technicians has been accomplished by manufacturer's representatives or prime contractors. This training was accomplished both before and during the operational phase of the weapon system. Without a capability to adequately train operational and maintenance personnel on a continuing basis, the Air Force must rely on assistance from contractors to maintain these

TABLE I

VAPOR DETECTION PRINCIPLES USED IN ICBM SYSTEMS

ICBM's	Fuel	Oxid	MAC Fuel/ Oxid (ppm)	LFL	Primary Hazards	Detection Systems Fuel	Oxid	Manufacturer
Atlas D, E, F Titan I	RP-1 and Diesel	LO_2	600/0	1.0%	Fire, Explosion	Thermal Conductivity	Depolarization Cell, Magnetic Thermal	MSA Hays Beckman Davis
Titan II	Aerozine 50	Nitrogen Tetroxide	.5/5	2-4.7%	Toxic, Fire	Infrared Ionization	Ionization	MSA

TABLE II

PRINCIPLES OF DETECTION

1. Catalytic
   Combustion
   Used to measure combustibles in the at-mosphere. A balanced electrical bridge contains a heated filament as one leg. When a combustible gas passes over this filament ignition results. This increases the temperature and resistance of the fila-ment. The bridge is thereby unbalanced. The resulting output voltage is calibrated in terms of percentage of combustibles in the sample.

2. Thermal
   Conductivity
   Used to measure both combustibles and non-combustibles in the atmosphere. Gases dif-fer in their heat conduction properties. Contaminants of the sample atmosphere will result in a different rate of heat conduc-tion as the sample is passed over a heated wire in the analysis cell. The resulting change of temperature of the wire will change its resistance. This will result in unbalanc-ing a bridge circuit which is calibrated in terms of concentration of some particular con-taminant in the sample.

3. Depolariza-
   tion
   Primarily for oxygen detection. This cell consists of a metal anode and a hollow electrode cathode encased in a container with suitable electrolyte. Due to electro-lytic action hydrogen ions form on the outer surface of the cathode. This tends to polarize the cell. When oxygen is in the sample it diffuses through the walls of the cathode and combines with the hydrogen ions thereby de-polarizing the cell. This permits a higher current output which is calibrated in terms of percentage of O_2 concentration.

4. Infrared Absorption

This method can be used for both oxidizer and fuel detection; however some substances transparent to infrared are not detectable. The principle depends on the absorption of infrared wavelengths by the particular gaseous contamination expected. An infrared beam passes into a gas cell with a flexible diaphragm "gas microphone" which moves as the gas expands and contracts. The beam from the sample and standard cell are "chopped" or alternately interrupted before entering the gas "microphone." If the sample contains contaminants, the instruments will read a fluctuation which is proportional to per cent concentration.

5. Ionization

This method can be used for both oxidizers and fuel. It is based on the capability of forming an "aerosol" with the gas in question. Reagents or burning processes can be found to react with a particular gas to form an aerosol (finely divided particulate matter). The aerosol decreases the ion current flow and thereby increases the resistance within the ionization chamber. This change in resistance is proportional to the percentage of contaminating vapor or gas in the sample.

6. Coulametric Titration

This method can be used for both oxidizer and fuels. The oxidizers however have to be weaker than the halogen used. When halogen in the electrolyte solution oxidizes the contaminating gas, its consumption will require additional current to restore the pre-set level. This additional current when calibrated indicates the quantity of combustible gas or oxidizer in the sample.

systems. Contractual training Air Training Command (ATC) instructors would provide an internal capability. ATC could maintain close liaison with contractors for new information that may affect training requirements.

3. Sample Representation and Identification of Area

a. Sample representation is also an important factor. A good representative sample is a problem where remote sniffers are used. For practical considerations the quantity of sniffer locations is limited. Each analyzer unit is used in conjunction with motor driven selector valves with a maximum of eight sniffer remote connections. Additional points would require additional analyzer units. Selector valves could be designed with additional connection points, however, this would increase the cycle time. Missile launch and propellant storage facilities take up vast amounts of space (100,000 - 200,000 ft^3). In this space, there may be numerous places where leaks are possible. Remote sniffers lose their effectiveness if not located near a leak point. Sniffer location would not be so critical if the space to be monitored was confined; however, these facilities can not be considered confined because of their enormous size and the provisions for air conditioning. The air conditioning systems induce flows which may carry vapors off in streams that by-pass sniffer locations. Installing separate miniature analyzers (see Appendix A3) or sniffer points in exhaust ducts might be of benefit; however, there is a counteracting dilution effect caused by the mixing of relatively large volumes of air with the vapor during air exchange cycles.

b. Although good representation of the over-all environment is desirable it is perhaps more important to pick up vapor near the leak point. In this way, the objective of identifying the location of the leak with increased responsiveness will be satisfied. Unfortunately, the cost of providing and installing the required number of sniffers can reach exorbitant levels. Until the cost per sniffer substantially decreases the location of sniffer points must be very carefully evaluated. The samples drawn off should be representative but at the same time the sniffers must be strategically located so that at least area identification is possible. A tape chemically treated for colorametric reaction with the vapor or liquid may alleviate the location problem. These tapes can be wrapped around possible leakage points permitting easy visual identification of the leak location.

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4. Responsiveness

When a change in concentration takes place, the time it takes for the analyzer to respond is primarily a function of the principle of detection. Various response times were given in the previous section. The inherent response times of themselves are a limitation; coupled with other factors (which extend the inherent response time) this renders the system useless as a warning device. A long sample line is a good example of a factor which can delay response time. A good rule of thumb is a response delay of one second for every 10 foot length of sampling line. Long sampling lines also tend to accumulate, collect, and trap condensed vapors particularly at low points and elbows. Furthermore, there is usually no provision for periodic blowdown of this contamination or condensate. The trapped condensate dissolves the sample vapor and levels out rapid changes in concentration. This dilution of the sample introduces additional response lags and inaccuracies.

5. Length of Sample Lines

Keeping sample lines as short as possible goes without saying; however, when facilities are greater than 150 feet in depth and 50 feet in diameter, short lines will not provide the required coverage. Short sampling lines (of less than 20 feet in length) are only possible if additional analyzer sets are provided. In effect, additional analyzers are the answer as they will permit additional sniffer points and shorter lines.

6. Validation of System

An analysis of the advantages of additional analyzers system-wise versus the disadvantages of increased buy, installation, and maintenance costs is beyond the scope of this study. A complete evaluation of this question, however, is an important step in detection system design. When a design is selected a testing program should be devised to validate the detection system. This program should be conducted under full scale conditions at a test site. For obvious reasons, it is extremely important that actual test establishes how these systems can perform under operational conditions. The test should also evaluate the training, tasks, skills, and spares necessary to keep this equipment in operational order.

7. Sensitivity and Selectivity

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a. Perhaps the most important factors in selecting a detection system principle are those of sensitivity and selectivity. The former indicates the capability of the method to detect a range of concentration-- a minimum to maximum per cent by volume of specific gas or vapor. The latter concerns the ability to detect a particular vapor or gas when several are present. Both factors are closely related.

b. In the ionization method selectivity for nitrogen tetroxide or aerozine (Titan II propellants) is excellent. The sensitivity of the method ranges from .05 parts per million to 200 parts per million. The ionization principle was a break through and has gained acceptance because of its capability to detect very small concentrations of toxic vapors. Due to its limited range, the infrared principle had to be employed to extend the range of the toxic fuel detection system (ionization principle). This requirement was probably specified because if the vapor level reached flammable concentrations (in the thousands of ppm), the hazard would be too great to permit the dispatching of emergency personnel to the missile silo. The infrared system was not sensitive enough to detect trace concentrations (1 ppm and less) of these propellants. The toxic hazard and the promptness of detection made it mandatory that the ionization principle be used. The need for quantitative information on combustible levels made it mandatory that an infrared principle be employed to detect larger concentrations of fuel vapor.

c. More than one principle may have to be used because of the sensitivity factor. This is undesirable because of the increased costs and problems associated with procuring, installing, and maintaining two different systems. Sensitivity must account for detection of the foreseeable ranges of vapor concentrations of the propellants involved. A case in point where this had not been considered important was with the rocket propellant fuel (RP-1) used on Atlas and Titan I missiles. RP-1 is a petroleum derivative composed of mixtures of various hydrocarbons. The detection systems principles selected (catalytic combustion and thermal conductivity) did not account for the low volatility of RP-1 and as a result were not sensitive enough to detect spills under ambient temperature conditions ($65^{o}F$). This was overlooked in the design of RP-1 and the diesel generator fuel detection systems. The fault lies in specifying a detection system based solely on detection of combustible levels. Therefore, it would be possible to lose complete containment of RP-1 fuel or diesel fuel

and not have detection. The undetected presence of this fuel is a dangerous fire hazard. Figure 1 shows a graph of RP-1 vapor pressure vs temperature. This graph points out that relatively high temperatures are required to reach the lower explosive level. Diesel fuels and hydraulic fluids have higher flash points and are less volatile than RP-1. Some other detection principle, for example, infrared absorption, could have provided the sensitivity needed to reliably detect the relatively low vapor levels of these substances at ambient temperatures as well as the high level of concentrations approaching the explosive levels.

d. A good example of how selectivity can become a problem (if not taken into consideration) is when the thermal conductivity principle is used. As previously mentioned thermal conductivity analyzers have been used on Atlas and Titan I missile systems for detection of RP-1 vapors in areas involved with transfer and storage. In order to simulate RP-1 vapor concentrations up to the Lower Explosive Limit the system was calibrated to respond to gases with thermal conductivities of less than that of air. Since nitrogen has a thermal conductivity less than air the detection system would respond to various concentrations of N_2 in the gas to be analyzed. There have been field incidents where an abnormal concentration of N_2 has caused this detection system to respond and in so doing has energized the purge and fog systems.

C. Future Developments

1. Area Sampling

Area sampling will overcome the limitations of point sampling insofar as assuring that a leak is detected. This is because the vapor is bound to pass through a large cross sectional area. The most obvious principle which can be used to provide area monitoring is one of the electromagnetic energy absorbing techniques. On the basis of over-all selectivity and sensitivity, infrared absorption is probably the most desirable method; however, ultraviolet or microwave may be more advantageous for certain applications. This method involves the use of an infrared beam of a particular wavelength range to monitor a fairly large open area. The infrared source is collimated, beamed and reflected over the area to be monitored. An arrangement of parabolic reflectors and optical lenses can be used to direct the beam from the source through the area to the detector located at the end of the beam
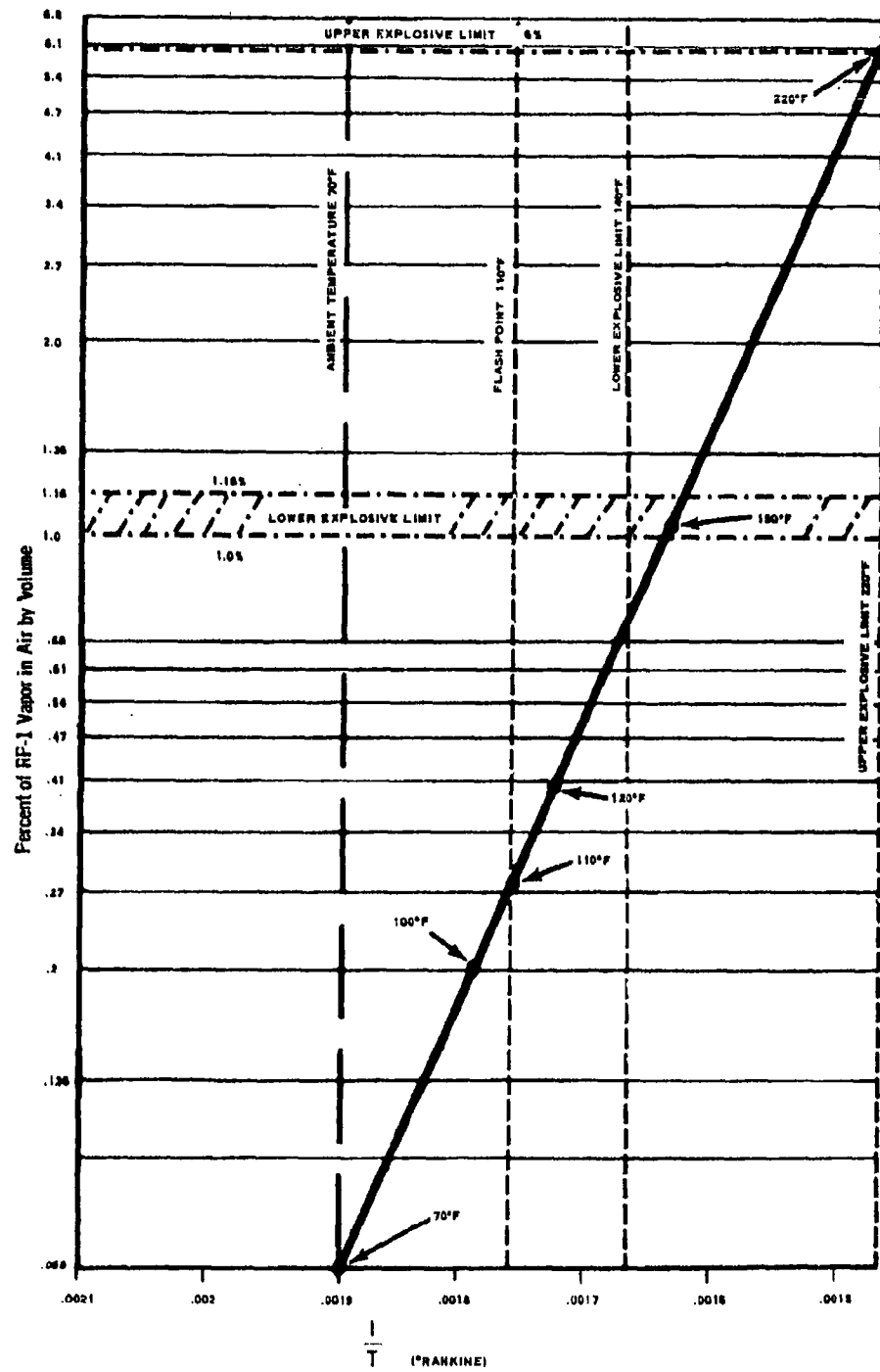
Figure 1. RP-1 Vapor Pressure vs Reciprocal of Absolute Temp.

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path. This design must be tailored to fit a launch facility and propellant storage area configuration. It can also be used to monitor the large open areas at or near missile test stands. A leak or spill will produce vapor that will pass through this zig zag open beam path and absorb energy. When this occurs it will be picked up, compared to a reference spectrum and amplified by the detection system.

The development of pickup systems to detect small energy changes is one of the greatest problems. As path length increases more molecules are available to absorb the energy; however, the intensity of the beam at the end of its path decreases (in proportion to the inverse square of the distance). With limited available power, the sensitivity of the pickup system becomes a critical factor. Another problem, the actual readout in an area sampling system of this type is an overall average, as the vapor will pass through only a portion of the sampling area.

2. Liquid Level Sensing

Probe assemblies consisting of several transducers mounted inside propellant and storage lines and tanks are used in missile systems to sense and control liquid level during fill and drain operations. The output signals from the transducers operate control valves, and propellant level indicating lights. The liquid level transducers now used on missile systems are of the filament, optic, capacitance, and oscillator types. Unfortunately, these systems were not designed to incorporate a remote warning spill or leak detection feature to indicate loss of containment. The hot filament, optics and capacitive methods are used for liquid oxygen and nitrogen systems.

a. The filament transducer contains a platinum wire which varies in resistance with temperature. When the sensor is covered with liquid the temperature change results in a change in resistance. This is detected by the control circuits which convert the signals into a relay output.

b. The optical type uses a light source directed by prisms to miss a photo electric cell detector. When the liquid intercepts the light source it is refracted; this deflects the beam sufficiently for detection by a photo electric cell.

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c. The capacitance sensing system consists of a probe with an inner electrode and outer tube. When dry this arrangement makes up a capacitor with an air or gas dielectric. When immersed or covered with a liquid, the dielectric changes produce an increase in capacitance that initiates a control circuit.

d. The oscillator type is used for both fuel and non-cryogenic oxidizers. An oscillating current is conducted to a pickup unit where it vibrates a crystal or sensing diaphragm in the sensor. With the crystal, the liquid acts to change the frequency of oscillation. This is compared to an identical crystal oscillation in the control unit and is amplified as an output signal. With the sensing diaphragm, the liquid contact acts to dampen the oscillation amplitude. When this occurs the feedback signal is insufficient to maintain oscillation.

e. All of the above systems are designed for installation within the missile, and storage tanks or pipe lines. With the exception of the capacitance type which can provide a continuous readout of liquid level, the systems described above are single point type probes. Indirect methods of liquid level sensing which do not depend on actual liquid contact with the sensor components are desirable. Therefore, all the equipment should be placed outside the containment vessel. The nuclear radiation type of senser is a good example of how this can be done. The source (a radioactive isotope) is located outside of the vessel as well as the detector. When the penetrating gamma rays pass through the walls of the vessel they are detected by a geiger counter or ionization cells on the opposite side. These cells are composed of dissimilar electrodes separated by a gas which is ionized when exposed to gamma radiation. This causes a flow of electrons or current. Intensity varies in proportion to the thickness of any material interposed between the source and the detector; thus, the liquid in the vessel will attenuate the radiation picked up by the detector. Less intensity results in a decrease in ionizing current which is sensed by the control circuitry. This system can be arranged for continuous or single point level detection. Installations must be made non-hazardous to operational and maintenance personnel. These systems provide high accuracy of measurement from ± 1/32 inch for non-cryogenics to ±1/16 inch for cryogenics. Other advantages are that the detectors are very stable, long leads can be used without loss of accuracy and the cells do not require an external voltage source.

APPENDIX A
DESCRIPTION OF VAPOR DETECTION PRINCIPLES

1. Thermal Conductivity

This principle has been widely adopted in gas and vapor detection equipment because all vapors and gases conduct heat to some degree. As the thermal conductivities of each gas differ it is a useful property for determination of the actual concentration of a gas or vapor in a mixture. Two identical hot wire cells mounted in the analyzer form adjacent branches of a wheatstone bridge. Each cell consists of a resistor mounted in a chamber containing a gas. The resistors are maintained at elevated temperatures by passing electric current through them. The sampling chamber contains the gas to be analyzed, and the comparison chamber contains the reference gas. The use of two chambers compensates for any differences in power input and ambient temperatures. If the atmosphere does not contain contaminating vapors the equilibrium temperature of both resistors is the same because the heating current is the same. When the sampling gas differs from the reference gas, however, the heat loss differs. This tends to change the equilibrium temperature (T) of the sampling chamber in proportion to the inverse of the thermal conductivity. This, in turn, changes the resistance of the sampling cell's heater element which results in an output signal from the wheatstone bridge circuit. (See Appendix B for description of wheatstone bridge circuits.) The heater element should have a high temperature coefficient of resistance so that a small change in equilibrium temperature can be measured in terms of a change in resistance. (Platinum is often used because of its large temperature coefficient and excellent chemical stability properties.)

There are many forms of these analyzers. Figure A1-1 depicts one of the basic designs. Most designs include the hot wire cells, a wheatstone bridge circuit, a bridge power supply, thermostat and heaters to reduce fluctuations in cell ambient temperature and filters, saturators, and dryers to condition the gas sample. The sensitivity of the analyzer cell is expressed in terms of the change of temperature of the wire to the change in thermal conductivity of the gas or vapor $\frac{(T)}{(K)}$. Analyzers can be built for full scale deflection when the thermal conductivity of the sample to the reference gas (usually uncontaminated air) is greater than 2 per cent. For example,

when O_2 in air reduces to 16 per cent the change in thermal conductivity is approximately 2 per cent. The full scale deflection would therefore be 16 per cent O_2 in air. For combustible gases or vapor full scale is set from 0 to 100 per cent of the lower flammability level (LFL) if possible. Sampling rates of over 1/2 cfm should be used to reduce response time to a minimum. Although calibration techniques are straightforward, it requires trained personnel and suitable facilities. Portable cylinders containing gases of known composition are passed through the cells and correlated with analyzer readings. Final adjustments and recalibration are done after installation in the field.

Figure A1 - 1

THERMAL CONDUCTIVITY PRINCIPLE
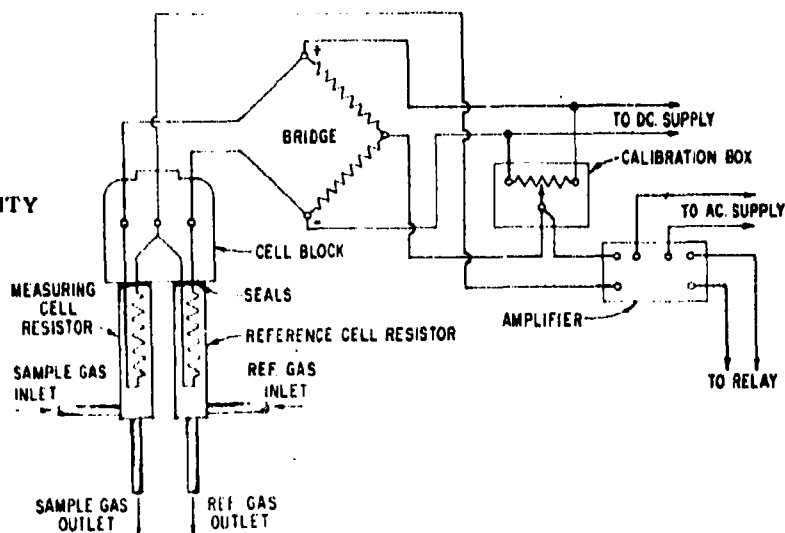
2. Catalytic Combustion

This principle is based on the fact that when a flammable gas or vapor is in the presence of a heated noble-metal filament a catalytic combustion process takes place.
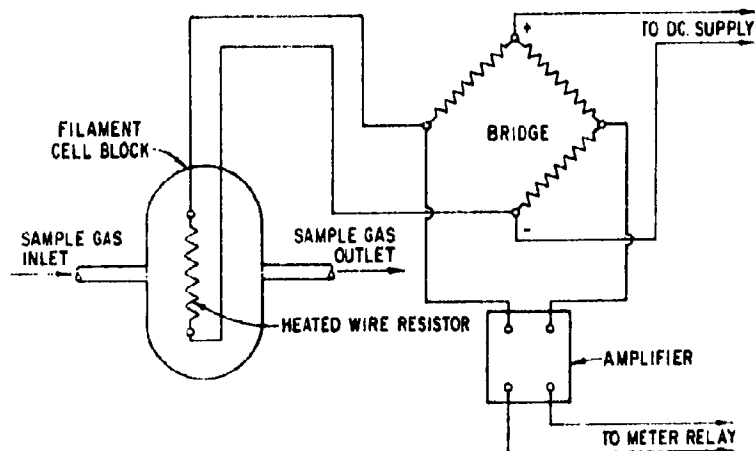
The method consists of passing the test sample over the heated catalytic filament. If the sample contains any combustible gases or vapors it will burn catalytically on

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the surface of this hot filament. This combustion will raise the filament temperature which in turn will increase its resistance. The heated filament is one leg of a wheatstone bridge circuit. The bridge supply voltage provides the power for heating the catalytic filament. Any variation in resistance of the filament due to heat of combustion will unbalance the bridge. A schematic of this method is shown in Fig A2-1. The output voltage of the bridge circuit is directional proportional to the concentation of combustible in the sample.

The range of these analyzers is set for full scale deflection from 0-100 per cent of the LFL limit of the combustible contaminant. For example, RP-1 detectors (see Chart I) are calibrated from 0-100 per cent LFL (the LFL of RP-1 is approximately 1 per cent by volume in air). The sensitivity of these instruments is approximately 1 per cent of full scale reading or in the order of 50-100 ppm for most combustibles. Where sensing of the glow intensity of the filament is picked up by a photo electric cell higher sensitivities may be achieved.

The discussion above on response time and calibration also applies to this method. This principle is also used in some oxygen analyzers. Hydrogen gas is metered into the cell and mixed with the sample gas. Combustion of the mixture (hydrogen and oxygen) takes place due to the initial temperature of the filament. The temperature rise and the resulting increase in resistance of the measuring filament is proportional to the amount of oxygen in the sample.

Figure A2 - 1

HOT FILAMENT
PRINCIPLE

FILAMENT
CELL BLOCK

TO DC. SUPPLY

BRIDGE

SAMPLE GAS
INLET

SAMPLE GAS
OUTLET

HEATED WIRE RESISTOR

AMPLIFIER

TO METER RELAY

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3. Depolarization

The principles described above may be used for combustible gases and vapors; this principle and the one which follows apply only to oxygen analyzers. Fig A3-1 illustrates a typical oxygen cell. This cell is a battery consisting of one metal anode and one hollow carbon electrode cathode housed in a plastic container filled with a liquid electrolyte with a relatively high ion concentration. When electric current is drawn from this cell the hydrogen ions being positive collect on the cathode. This causes a back electromotive force (emf) or polarization which depresses the output voltage of the cell and reduces the current to zero. A sample of the atmosphere is passed through the tubular core of the cathode. If oxygen is present in the sample it diffuses through the porous walls to the outer surface of the electrode where it reacts with the hydrogen ions. This decreases the back emf (depolarization) which increases the cell output in proportion to the oxygen concentration. This output signal is calibrated in terms of per cent O_2 in air. Known mixtures of oxygen and nitrogen are used and the meter deflection is adjusted accordingly. Standard ranges are from 0-40 per cent O_2 in air. The response time of the cell is in seconds. A miniature device recently developed eliminates the use of the liquid electrolyte, (liquid electrolyte has to be periodically added to detector cells) and the need to replace the carbon electrodes. The cell consists of a platinum cathode and silver anode surrounded by a potassium chloride gel. A gas permeable membrane fits against the platinum electrode surface. When oxygen passes through this membrane it is electrically reduced by an applied potential causing a current flow which is directly proportional to the concentration of O_2 in the sample. The entire cell is replaced periodically. This device is designed to be located in ductwork or flow streams which eliminates the need for a vacuum pump for drawing samples from point sniffers through tubes to the cell. The analyzer can be electrically connected to remote warning indicators. The range of the device can be calibrated from 0-100 per cent of O_2; the response time is in seconds.

4. Paramagnetic Thermal

Oxygen, nitrogen oxide and dioxide are unique in that they are paramagnetic (attracted to a magnetic field). The magnetic susceptibility of these molecules decreases rapidly with temperature. Both of these properties are used to advantage in the design of oxygen detection cells.
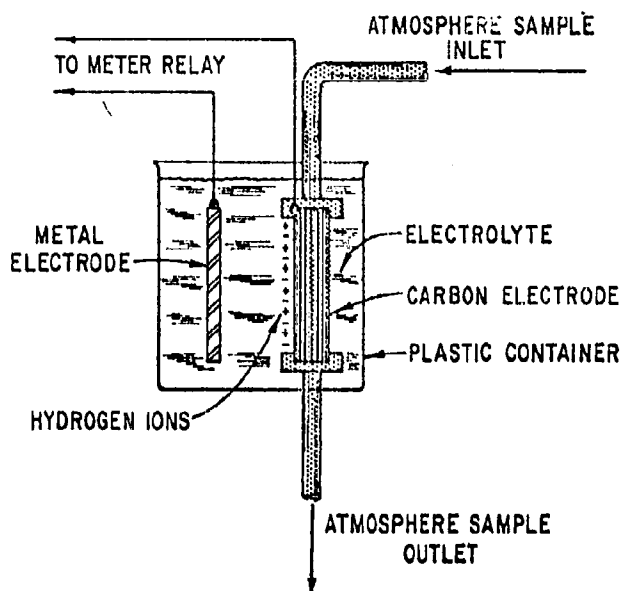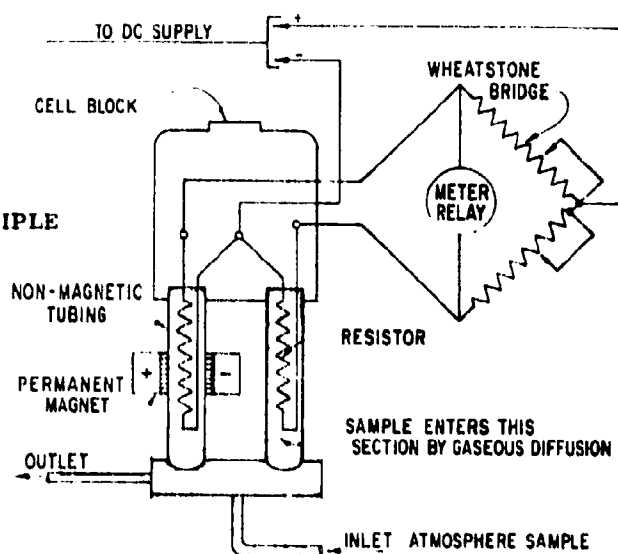
Fig. A3-1

The analyzing cell consists of two chambers with identical electrically heated resistors. These form the two branches of a wheatstone bridge circuit. When the permanent magnet (which is hinge mounted) is in the zero or non-analyzing condition, the sample gas diffuses upward into the two chambers (see Fig A4-1). Since the wires, heating conditions, etc., are identical there will be no measured difference in the resistances. If, however, the permanent magnet is swung into position so that one of the heater elements (the measuring cell) is located in a region of high magnetic flux, the oxygen in the sample will be attracted to that region. As the oxygen is heated it loses its magnetic properties and is displaced by cooler oxygen. This causes a magnetically induced thermal circulation or convection which results in additional cooling of the heater wire in the measurement cell greater than in the referenced cell. The differences in temperature are proportional t, the magnetic susceptibility of the gas. This results in a difference in resistances which produces a voltage unbalance in the bridge circuitry. This output signal is proportional to the oxygen content of the gas sample. The instrument is adjusted to read zero with the magnet swung out. Fresh atmospheric air is admitted, the magnet placed in operating position, and the instrument is calibrated so that the indicator reads 20.7 per cent O_2. Other readings are checked in the same manner with known gas mixtures. In general initial response

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TO DC SUPPLY

WHEATSTONE BRIDGE

CELL BLOCK

METER RELAY

Figure A4 – 1

MAGNETIC THERMAL PRINCIPLE

NON-MAGNETIC TUBING

RESISTOR

PERMANENT MAGNET

SAMPLE ENTERS THIS SECTION BY GASEOUS DIFFUSION

OUTLET

INLET ATMOSPHERE SAMPLE

to a change in oxygen concentration is in seconds with flow rates of about 0.5 cfm; final response occurs in less than one minute.

Another method utilizing this principle measures the paramagnetic susceptibility of the sample by determining the change of the magnetic flux acting on a test body. If the sample gas surrounding the test body is more or less paramagnetic the test body will be displaced toward the region of maximum flux densities. The greater the concentration of O_2 the greater will be the rotation of the test body. The rotation of the test body is balanced by the torsional restoring force of a quartz fiber. A beam of light reflected from a mirror attached to the quartz fiber is deflected in proportion to the rotation of the the test body. The oxygen concentration is read by observing the position of the light on a calibrated translucent scale. These instruments can be calibrated in ranges up to 100 per cent O_2. The above is suited to a portable device, however, a null-type meter for continuous recording applications is also available. An electrical potential is automatically varied in accordance with the electrical field required to hold the test body in the null position (counteract the magnetic force). This potential is a direct measure of the gases surrounding the test body. The calibration of these devices are strictly linear (only two points on the scale such as an oxygen free gas and dry air will suffice to calibrate these devices).

22

5. Ionization

This principle utilizes the chemical properties of gas ionization and the current decreasing effect of an aerosol (finely divided particulate matter). Figure A5-1 depicts an ionization chamber. A radioactive source will cause a current flow in a gas proportional to the strength of the source, the ionizing potential (the voltage between the electrodes) and the mobility and recombination of the ions in the gas. When air is introduced into the chamber a slight current will flow due to the affinity of O_2 molecule in the air for electrons. Contamination in the air even in the thousands of parts per million has negligible effect on the magnitude of this ion current. A small amount of aerosol, however, will increase the ion recombination rate through third body collisions and decrease ion mobility by attachment. The effect of this is to increase the resistance within the ionization chamber and thereby decrease the current flow. This change of resistance is proportional to the concentration of the trace material to be analyzed. It should be pointed out that the contaminating vapor or gas can only be detected if a suitable reagent or process such as pyrolyses (burning or irradiation) can be found to convert it to an aerosol. When such method can be found high selectivity and sensitivity is achieved. For example the table on the next page indicates the preferred methods used for some very toxic substances. The propellant combination for the Titan II consists of the last three items in the table. The other chemicals are being tested for possible future applications as rocket propellants.

The ionization chamber is made as one arm of a wheatstone bridge type of circuit. A reference chamber makes up the other arm of the bridge. The ion current at a preselected voltage is compared to that in the reference chamber. When the sample does not contain the specified contaminant (normal air) the bridge is balanced. If, however, there is a sufficient trace of the contaminant, it will react with the reagent to form an aerosol. The resulting increase in resistance will unbalance the circuit. The output signal can be fed to a meter calibrated in terms of the detected compound. The response of this method is rapid (in seconds). Figure A5-2 illustrates several typical arrangements.

Material Fuels & Oxidizers	MAC (ppm) Fuel or Oxid	MAC(ppm) Reagent	Scale Sensitivity Ranges		Minimum Detectable Signal	Chemical Reagent and/or Pyrolyses
			Min	Max		
HF Hydrogen Fluoride	3.0	100	0-2	0-200	.1	NH_3 Reagent
F_2 Fluorine	.1	100	0-2	0-200	.1	"
CLF_3 Chlorine Triflouide (CTF)	.1	100	0-2	0-200	.1	"
B_5H_9 Penta-borane	.005		0-0.2	0-20	.01	Pyrolysis with n-Amylamine reagent
N_2H_4 Hydrazine	1.0	5	0-1	0-100	.05	Nitrogen trioxide NO_3 reagent
UDMH $(CH_3)N_2H_2$	.5		0-2	0-200	.1	"
NO_2 Nitrogen Dioxide	5.0	25	0-5	0-300	25	Dimethylamine anyhdrous

SUBJECT: Errata Sheet for Study Nr. 39-63, Missile
           Vapor Detection Systems

     TO: Distribution List

          The following corrections, additions or deletions
     should be made to Study Nr. 39-63.

          a.   On first page after the cover write in the
     date, 1 Sep 63, under the study number.

          b.   Page 17.   Place small triangle (symbol for
     change) before the (T) and (K) in the quotient $(\frac{T}{K})$.

          c.   Page 26.   Delete the fifth sentence, "The
     percentage of energy loss can be measured." Add the
     words, "percentage of" in between the words "the" and
     "energy loss" in the fourth sentence.

          d.   P. 27, para 4, sentence 4.   After words "as
     shown" delete the word "above" and replace with
     "in Fig A6-2."

          e.   P. 28, Fig A6-2.   After the first arrow
     place a sub-zero under the I to designate incident
     energy (I_0). Near the arrow emerging from the rectangle
     write in the letter "I" to designate emergent energy.

          f.   P. 32.   On top of page write in "APPENDIX B."
     Under that write in "TYPICAL WHEATSTONE BRIDGE."

          g.   P. 33.   On top of page write in "APPENDIX C."
     The word "connection" in the definition of equilibrium
     temperature should be "convection."

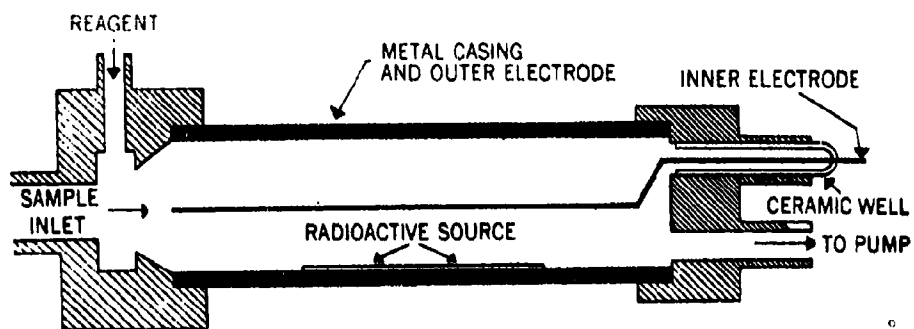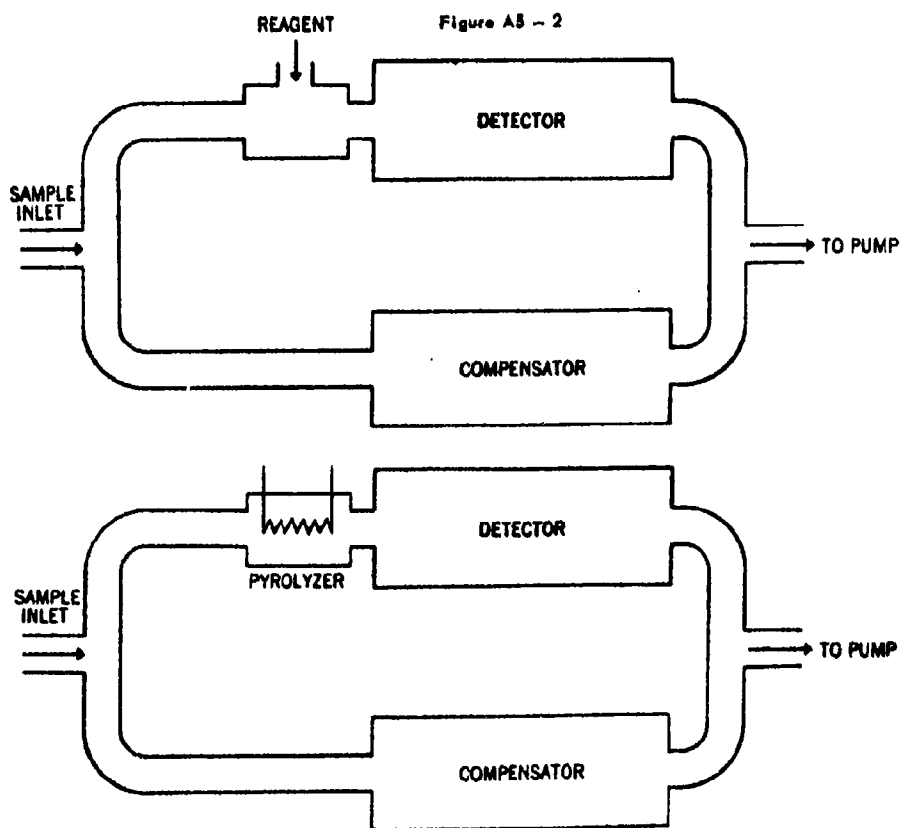   h.   P. 35.   On top of page write in "APPENDIX D."

REAGENT

METAL CASING
AND OUTER ELECTRODE

INNER ELECTRODE

SAMPLE
INLET

RADIOACTIVE SOURCE

CERAMIC WELL

TO PUMP

Figure A5 — 1

Figure A5 — 2

REAGENT

DETECTOR

SAMPLE
INLET

TO PUMP

COMPENSATOR

DETECTOR

SAMPLE
INLET

PYROLYZER

TO PUMP

COMPENSATOR

25

6. Infra Red Absorption

Many polyatomic compounds have the ability of absorbing a certain percentage of electromagnetic radiation in the infrared region (between 1-25 microns). This occurs when a molecule is exposed to specific frequencies within this range. Each molecule has distinct infrared frequencies of vibration in which it absorbs energy and then vibrates or rotates. By using a suitable infrared detector the energy loss can be measured. The percentage of energy loss can be measured. The percentage of energy loss is proportional to the number of gas molecules (concentration) which were made to vibrate. Infrared spectrophotometers measure the amount of absorption of a given sample as a function of wavelength. The transmittance is the ratio of the energy leaving the sample to the energy of the wavelength entering the sample in terms of per cent. The per cent transmittance plotted as a function of wavelength is the infrared spectrogram of the molecule. The importance of this method from a detection standpoint is that the spectrum of each compound is unique. Figure A6-1 below shows the vapor absorption characteristics of UDMH and Nitrogen Trioxide. As long as the differences in absorption are sufficiently marked it is possible to determine a small percentage of one gas in the presence of another. The

Figure A6-1   INFRARED FINGERPRINTS OF UDMH AND N_2O_4
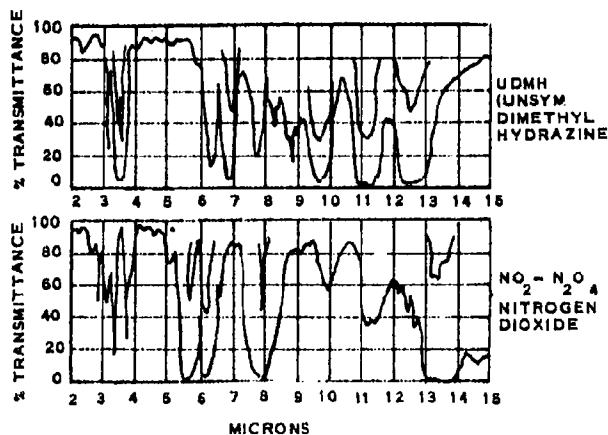
degree to which an infrared detection system can detect the difference between two such gases in a sample is referred to as "selectivity." Certain gases, however, such as hydrogen, nitrogen, and the halogens do not absorb infrared energy.

A good estimate of energy I of a given infrared wave after gas absorption is given by the Lambert-Beer Law: $I = I_0 e^{-kpcl}$. In sensitizing, wave lengths are selected where the desired component absorbs strongly and all others are transparent.

The schematic of a simple system, Figure A6-2 explains the variables and constants in the equation.

For gases that have a high (k) a smaller concentration may be detected for a given path length (l). Also of significance is the fact that the sensitivity of this method increases with smaller concentrations; that is I/C increases at a faster rate at the lower I_0 concentrations because of the exponential nature of Beer's law. Sensitivity also increases with path length because more molecules are available to absorb the radiation. As shown above when a gas is present I_0 is reduced to I. By subtracting both sides of the equation by I_0 and dividing by I_0 we have $\frac{I_0-I}{I_0} = 1 - e^{-kpcl}$. Multiplying

both sides by 100 the total per cent absorbed (A) is $\frac{100(I_0-I)}{I_0} = \%A = 1 - e^{-kpcl}$.

As gas concentration increases more energy is absorbed by the gas. This, in turn, causes less energy I to reach the detector. Since the detector is sensitive to diminishing energy levels, an increase in gas concentration will provide a proportional signal output from the detector. In order to obtain an infrared spectrum of a gas various wavelength bands must be selected from a wide band infrared source. This is done by: separating the source into component wavelengths with prisms or a grating; reflecting all but the desired band with bandpass interference filters or using gases sealed in a chamber to absorb certain wavelengths. The latter method is used with continuous infrared detectors of the negative and positive type. In the negative type, infrared energy split into two equal beams passes through a sample cell into a filter cell and a compensator cell. The gas or vapor that the detector is sensitized for, is sealed within the filter cell.
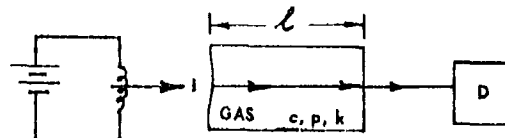
- e – base of natural logar-
  ithms – 2.718
- I₀ – incident energy
- I – Emergent energy
- l – path length

- c – concentration % volume
- p – Absolute pressure
- k – absorption coefficient
  of gas

The filter cell removes all of the infrared energy at the
wavelengths of absorption of the gas to be detected.
If the sample gas mixture contains this gas, beam #1 is
not affected (see Figure A6-3). However, beam #2 rises
and falls in total energy as the sample concentration
changes (the compensator cell is filled with an inert
gas insensitive to infrared energy). Energy sensors
(bolometer or thermopile) are shown which provide an
electrical output. This signal, a measure of the difference
in energy between the beams, can be calibrated in terms of
the sample concentration.

The positive type of infrared detector is similar in
design, but uses a "gas microphone" to translate the
energy received into an output signal. Two nichrome wire
helices are electrically heated (see Figure A6-4) to emit
parallel infrared energy beams. One beam traverses the
sample cell, the other beam the comparison cell. A rotat-
ing interceptor or chopper alternately blocks the radiation
entering the two cells. When the beams are equal, an
equal amount of energy enters the "gas microphone" detector.
As the gas in the detector absorbs this energy, its
pressure increases causing the membrane (a flexible metal
diaphragm) of the condenser microphone to move with uni-
form intensity at the "chopper" frequency. The membrane
forms one element of a charged capacitor. An amplifier
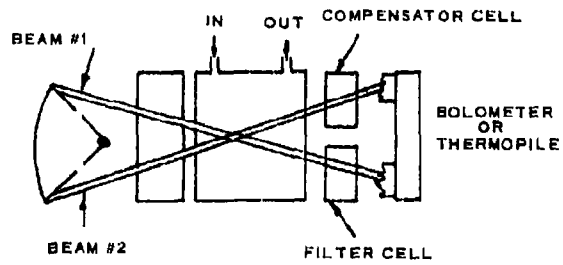
NEGATIVE TYPE FILTER INFRARED ANALYZER
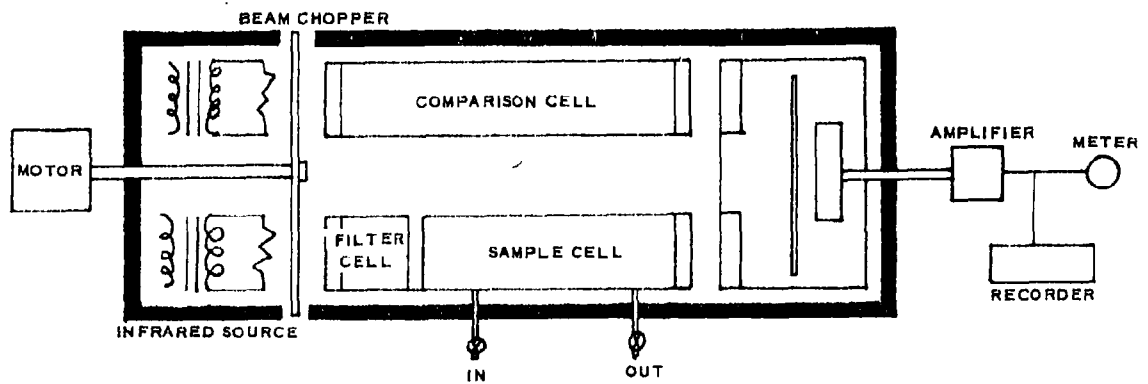

Figure A6-3

POSITIVE TYPE INFRARED ANALYZER

Figure A6-4

is tuned so that only variations in infrared intensity will produce an output signal. The detector therefore reads zero when the beams are equal. When, however, the gas to be analyzed is passed through the sample cell it absorbs some infrared which reduces the radiation reaching the detector. This results in a variation in membrane movement which changes the capacity of the condenser and generates an electrical signal proportional to the difference between the two radiation beams.

Similar equipment is made using an ultraviolet source (200-400 millimicrons). In most cases ultraviolet energy is more sensitive but less selective than infrared. Ultraviolet and visible spectra will identify the atoms of a molecule, whereas infrared can identify functional groups. Ultraviolet is strongly responsive to elemental halogen vapors and to ozone (infrared is completely insensitive to these molecules). The basic ultraviolet analyzer consists of a radiation source, optical filters, sample cell and an output meter. (See Fig A6-5).
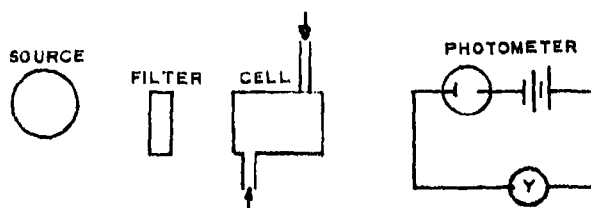

Figure A6-5   Basic Ultraviolet Detector

Vacuum phototubes are used as ultraviolet detectors. Accuracies are obtainable within 1 per cent of full scale readings for both infrared and ultraviolet detectors. Response to changes in concentration is less than a minute.

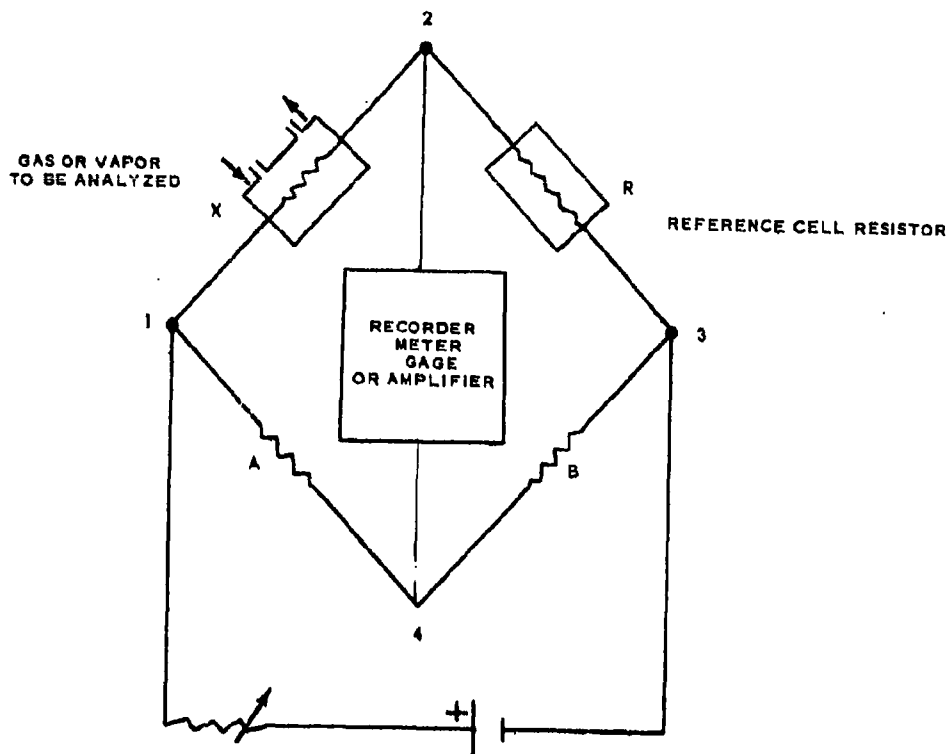Microwave (1mm - 30 cm wavelength) detectors are also being developed where positive identification of specific compounds is possible. The interaction of a unique microwave frequency with a molecule of vapor will result in its partial absorption by the molecule. This energy can also be detected and measured by electronic methods.

7. Coulametric Titration

Coulametric analyses involve the determination of

30

current flow through an electrolyte. This flow is directly proportional to the number of active ions present in solution as well as to such factors as the voltage across the electrodes, the resistance of the solution and the temperature. Two pairs of electrodes termed sensing and generating, serve to maintain a current flow and generate the halogen in the electrolyte. When the halogen ions are converted to gas at the generating electrodes, they lose electrons. The hydrogen ions at the cathode accept these electrons; the resulting hydrogen gas is passed off with air being bubbled through the electrolyte. At the sensing electrodes a thin film of hydrogen polarizes the cathode. The presence of the halogen, however, permits a small current flow (the halogen reacts with the hydrogen which depolarizes the cell). If the halogen concentration is reduced by its reaction with fuel vapor, current flow is stopped. The sensing electrodes detect this change causing a feedback servo device to increase the voltage at the generating electrodes. This tends to keep the cell depolarized and the level of free halogen in solution constant. The current at the generating electrode can therefore be calibrated in terms of the concentration of the reducing material (fuel vapor) in the air stream. The response time is less than 1/2 minute with sensitivities as low as .05 parts per million.

The oxidizer detector is similar to the fuel detector except that generating electrodes are not required. When an oxidizer enters the cell the halogen ions in solution are oxidized. The gas which evolves is sensed by the cell's electrodes. This destroys the equilibrium and results in a current flow proportional to the concentration of oxidizer in solution.

·

GAS OR VAPOR
TO BE ANALYZED

2

X

R

REFERENCE CELL RESISTOR

1

3

RECORDER
METER
GAGE
OR AMPLIFIER

A

B

4

+

When the bridge is balanced points 2 and 4 are at the same potential (voltage drop across X and A are the same). Any change in the resistance of X will upset the balance of the bridge resulting in an output signal across 2,4. This occurs only when the sample gas introduced into X causes a difference in temperature or temperature rise between X and R. The condition of heating current $i_{1,2} = i_{2,3}$ remains approximately the same because of the high impedance across 2,4. This permits a continual comparison between X and R based only on the constituents of the sample vapor.

GLOSSARY OF TERMS

Aerosol — Finely dispersed airborne particle.

Abnormal Presence — When the hazardous substances are no longer contained in the vessel or tank.

Bolometer — A device which changes its electrical resistance with temperature in response to the intensity of radiation falling upon it.

Catalytic Combustion — The burning of a fuel on the surface of a catalytic agent such as a hot platinum filament. The platinum catalyst acts to induce oxidation below the Lower Flammability Limit.

Chopper — Any device used to interrupt a continuous current, flux or beam.

Drift — The deviation of the instrument indication with time. This occurs because of aging of electrical components.

Equilibrium Temperature — The steady state temperature which results when the electrical power input to a wire is equalized by all thermal losses from the wire; thermal losses include those due to gaseous conduction, connection, radiation and conduction through the support of the wire.

LFL and UFL — The lower and upper flammability limits designate the lowest and highest percentages (by volume) of a combustible gas or vapor air mixture which will burn continuously when ignited by an outside source.

MAC — The maximum allowable concentration is given in parts of vapor or gas per million parts of air (ppm) by volume at 77°F and standard atmospheric pressure. It specifies the maximum ppm of a substance that a non-allergic person can be exposed to continuously (40 hr week over a normal working lifetime) without injury to health.

Micron — One millionth of a meter.

Monatomic   —   Having one atom in the molecule.

Polyatomic   —   Having several atoms in the molecule.

Response time —   The time required for a device or system
                         to detect a specified percentage of the
                         total change it will make, due to a
                         measurable change in the substance being
                         analyzed.

Responsiveness —   The ability of a system to follow
                         changes in value of the measured quantity.

Selectivity   —   That characteristic of a detection
                         principle which determines the extent
                         to which it can differentiate between
                         various substances.

Sensitivity   —   The least signal input capable of causing
                         an output signal having the desired
                         characteristics.

Temperature Coefficient of Resistance —

                         The change in resistivity of a conductor
                         for each unit change in temperature.

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